

## CLAIMS

1. A crystalline layered compound characterized in that the chemical composition of which is represented by  $[(\text{Si}_{18-x}\cdot\text{O}_{38}) \cdot \text{M}_y \cdot (\text{TMA})_z \cdot (\text{H}_2\text{O})_w]$  (wherein TMA is a tetraalkylammonium cation, M is a cation of an alkali metal such as, Na, K or Li, x satisfies  $0 \leq x \leq 1.2$ , y satisfies  $0.5 \leq y \leq 1.5$ , z satisfies  $6 \leq z \leq 8$ , and w satisfies  $0.02 \leq w \leq 1.5$ ), having as the basic structure thereof a single-layer skeleton comprising one-dimensional micropores nanometers in size formed by a network of covalent bonds between Si and O atoms, the lattice spacing d in the powder x-ray diffraction pattern being at least as described in Table 7 below (wherein d is the lattice spacing, w = weak relative strength, m = moderate relative strength, s = strong relative strength and vs = extremely strong relative strength).

Table 1

d(Å)	Relative strength
10.47±0.2	vs
8.38±0.15	w
7.34±0.15	m
7.00±0.1	m
6.51±0.1	m
6.45±0.1	s

$5.86 \pm 0.05$	m
$5.82 \pm 0.04$	m
$5.66 \pm 0.04$	w
$5.23 \pm 0.04$	m
$5.07 \pm 0.04$	w
$4.90 \pm 0.04$	s
$4.75 \pm 0.04$	m
$4.57 \pm 0.04$	w
$4.40 \pm 0.04$	m
$4.35 \pm 0.04$	s
$4.26 \pm 0.04$	s
$4.19 \pm 0.04$	vs
$4.00 \pm 0.04$	m
$3.94 \pm 0.035$	s
$3.85 \pm 0.035$	s
$3.83 \pm 0.035$	vs
$3.78 \pm 0.035$	w
$3.67 \pm 0.035$	m
$3.63 \pm 0.035$	s
$3.60 \pm 0.035$	w
$3.55 \pm 0.035$	m
$3.51 \pm 0.035$	m
$3.50 \pm 0.035$	vs
$3.48 \pm 0.035$	vs
$3.38 \pm 0.035$	m
$3.34 \pm 0.035$	w

3.32±0.035 s

2. The crystalline layered compound according to Claim 1, wherein in the layered compound the local coordination of the O atoms surrounding the Si atoms in the Si-O network is tricoordinate and tetracoordinate.

3. The crystalline layered compound according to Claim 1, wherein in the layered compound alkali metal cations and an organic structure directing agent are included in the gaps between layers of the crystal structure.

4. The crystalline layered compound according to Claim 1, wherein in the layered compound the effective gap between layers is 3 Å or more.

5. The crystalline layered compound according to Claim 1, wherein the layered compound has pores formed of skeletal sites which are silicon 5-member rings or larger.

6. A method for manufacturing a crystalline layered compound characterized by comprising heating a crystalline layered compound in the presence of an organic structure directing agent, to synthesize a crystalline layered compound with the chemical composition represented by  $[(\text{Si}_{18-x}\cdot\text{O}_{38}) \cdot \text{M}_y \cdot (\text{TMA})_z \cdot (\text{H}_2\text{O})_w]$  (wherein TMA is a tetraalkylammonium cation, M is a cation of an alkali metal such as Na, K or Li, x

satisfies  $0 \leq x \leq 1.2$ ,  $y$  satisfies  $0.5 \leq y \leq 1.5$ ,  $z$  satisfies  $6 \leq z \leq 8$ , and  $w$  satisfies  $0.02 \leq w \leq 1.5$ ).

7. The method for manufacturing a crystalline layered compound according to Claim 6, wherein a crystalline layered compound defined in any of Claims 1 through 5 is synthesized.

8. The method for manufacturing a crystalline layered compound according to Claim 6 or 7, wherein the organic structure directing agent is at least one selected from tetramethylammonium salts, tetraethyl ammonium salts, tetrapropylammonium salts, tetrabutylammonium salts and other quaternary alkylammonium salts and amines.

9. A zeolite characterized by having the chemical composition represented by  $[(\text{Si}_{36-x}\text{T}_y \cdot \text{O}_{72}) \cdot \text{M}_2]$  (wherein  $\text{M}$  is a cation of an alkali metal such as  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$  or  $\text{Rb}$ ,  $\text{T}$  represents  $\text{Al}$ ,  $\text{Ga}$ ,  $\text{Fe}$  and  $\text{Ce}$  as skeleton substituting elements,  $x$  satisfies  $0 \leq x \leq 3.0$ ,  $y$  satisfies  $0 \leq y \leq 1.0$ , and  $z$  satisfies  $0 \leq z \leq 3.0$ ), and having a micropore structure made up of covalent bonds between  $\text{Si}$  and  $\text{O}$  atoms.

10. The zeolite according to Claim 9, wherein the lattice spacing  $d$  ( $\text{\AA}$ ) in the powder x-ray diffraction pattern is as described in Tables 2 and 3 below.

Table 2

d(Å)	Relative strength
9.17±0.05	100
6.86±0.05	35
6.11±0.05	5
5.50±0.05	4
4.84±0.05	1
4.70±0.05	1
4.58±0.05	3
4.44±0.05	7
4.35±0.05	7
4.09±0.05	6
3.88±0.05	8
3.81±0.05	9
3.68±0.05	3
3.43±0.05	25
3.41±0.05	29
3.31±0.05	8
3.24±0.05	9
3.07±0.05	1

Table 3

d(Å)	Relative strength
9.25±0.05	100
8.85±0.05	7
7.67±0.05	4
6.85±0.05	65

6.14±0.05	7
4.74±0.05	6
4.65±0.05	7
4.49±0.05	13
4.40±0.05	5
4.10±0.05	5
3.90±0.05	7
3.84±0.05	8
3.71±0.05	5
3.44±0.05	30
3.34±0.05	14
3.26±0.05	9
3.08±0.05	4
2.99±0.05	3
2.89±0.05	2
2.75±0.05	1
2.37±0.05	2
1.97±0.05	2
1.86±0.05	2

11. The zeolite according to Claim 9, wherein the crystal structures can be described as orthorhombic with crystal lattice constants in the range of  $a = 18.35 \pm 0.05 \text{ \AA}$ ,  $b = 13.77 \pm 0.03$ ,  $c = 7.37 \pm 0.03 \text{ \AA}$  (space group Pnma), orthorhombic with lattice constants in the range of  $a = 18.35 \pm 0.05 \text{ \AA}$ ,  $b = 13.77 \pm 0.03$ ,  $c = 7.37 \pm 0.03$

Å (space group Pnnm), orthorhombic with lattice constants in the range of  $a = 18.35 \pm 0.05$  Å,  $b = 13.77 \pm 0.03$ ,  $c = 14.74 \pm 0.03$  Å (space group Pbcm) and monoclinic with lattice constants in the range of  $a = 18.35 \pm 0.05$  Å,  $b = 13.77 \pm 0.03$ ,  $c = 7.37 \pm 0.03$  Å,  $\beta = 90 \pm 0.3^\circ$  (space group P21/m).

12. The zeolite according to Claim 9, wherein the local coordination of the O atoms surrounding the Si atoms in the skelton structure is tetracoordinate.

13. The zeolite according to Claim 9, wherein the skeletal structure formed by the binding of the Si and O atoms has a regular geometry.

14. The zeolite according to Claim 9, having pores with a mean size of 0.48 nm or more due to gas adsorption.

15. A method for manufacturing a zeolite characterized by performing dehydration polycondensation of the crystalline layered compound defined in Claim 1, to synthesize a zeolite with the chemical composition represented by  $[(Si_{36-x}T_y \cdot O_{72}) \cdot M_2]$  (wherein M is a cation of an alkali metal such as Li, Na, K or Rb, T represents Al, Ga, Fe and Ce as skeleton substituting elements, x satisfies  $0 \leq x \leq 3.0$ , y satisfies  $0 \leq y \leq 1.0$  and z satisfies  $0 \leq z \leq 3.0$ ).

16. The method for manufacturing a zeolite according to Claim 15, wherein manufacture is in a vacuum

in the range of  $1 \times 10^{-3}$  to  $1 \times 10^{-8}$  torr as a condition for dehydration polycondensation.

17. The method for manufacturing a zeolite according to Claim 15, wherein the heating temperature for dehydration polycondensation is 400 to 800°C.

18. The method for manufacturing a zeolite according to Claim 15, wherein the zeolite is manufactured at atmospheric pressure as a condition for dehydration polycondensation.

19. The method for manufacturing a zeolite according to Claim 15, wherein the heating temperature for dehydration polycondensation is 300 to 800°C.

20. The method for manufacturing a zeolite according to Claim 15, wherein the rate of temperature rise is 0.5 to 50°C per minute.

21. The method for manufacturing a zeolite according to Claim 15, wherein as a combustion-supporting gas a gas comprising oxygen molecules in a molecular state is used.

22. A catalyst or separation/adsorption material comprising the zeolite according to any of Claims 9 through 14.

23. A zeolite membrane characterized by comprising a zeolite (CDS-1) formed as a membrane on a support, said zeolite having the chemical composition represented by  $[(\text{Si}_{36-x}\cdot\text{O}_{72})\cdot\text{M}_y]$  (wherein M is a cation of an alkali metal



such as Na, K or Li,  $x$  satisfies  $0 \leq x \leq 3.0$ ,  $y$  satisfies  $0 \leq y \leq 3.0$ ) and a micropore structure made up of covalent bonds between Si and O atoms, with a silicate structure of repeating units of Si-O tetrahedral coordination and geometrical crystal structures (atomic arrangement) comprising silicon 5-member and 8-member rings.

24. The zeolite membrane according to Claim 23, wherein said crystal structures are (1) orthorhombic with crystal lattice constants in the range of  $a = 18.35 \pm 0.05 \text{ \AA}$ ,  $b = 13.77 \pm 0.03$ ,  $c = 7.37 \pm 0.03 \text{ \AA}$  (space group Pnma), (2) orthorhombic with lattice constants in the range of  $a = 18.35 \pm 0.05 \text{ \AA}$ ,  $b = 13.77 \pm 0.03$ ,  $c = 7.37 \pm 0.03 \text{ \AA}$  (space group Pnnm), (3) orthorhombic with lattice constants in the range of  $a = 18.35 \pm 0.05 \text{ \AA}$ ,  $b = 13.77 \pm 0.03$ ,  $c = 14.74 \pm 0.03 \text{ \AA}$  (space group Pbcm) and (4) monoclinic with lattice constants in the range of  $a = 18.35 \pm 0.05 \text{ \AA}$ ,  $b = 13.77 \pm 0.03$ ,  $c = 7.37 \pm 0.03 \text{ \AA}$ ,  $\beta = 90 \pm 0.3^\circ$  (P21/m).

25. The zeolite membrane according to Claim 23, wherein the lattice spacing  $d$  ( $\text{\AA}$ ) in the powder x-ray diffraction pattern is at least as described in Tables 4 and 5.

Table 4

$d(\text{\AA})$	Relative strength (peak)
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9.17±0.05	100
6.86±0.05	35
6.11±0.05	5
5.50±0.05	4
4.84±0.05	1
4.70±0.05	1
4.58±0.05	3
4.44±0.05	7
4.35±0.05	7
4.09±0.05	6
3.88±0.05	8
3.81±0.05	9
3.68±0.05	3
3.43±0.05	16
3.41±0.05	18
3.31±0.05	8
3.24±0.05	9
3.07±0.05	1

Table 5

d(Å)	Relative strength (peak)
9.25±0.05	100
8.85±0.05	7
7.67±0.05	4
6.85±0.05	65
6.14±0.05	7

4.74±0.05	6
4.65±0.05	7
4.49±0.05	13
4.40±0.05	5
4.10±0.05	5
3.90±0.05	7
3.84±0.05	8
3.71±0.05	5
3.44±0.05	30
3.34±0.05	14
3.26±0.05	9
3.08±0.05	4
2.99±0.05	3
2.89±0.05	2
2.75±0.05	1
2.37±0.05	2
1.97±0.05	2
1.86±0.05	2

26. The zeolite membrane according to Claim 23, wherein the support is a porous base of an inorganic porous body, metal or metal oxide.

27. A zeolite membrane manufacturing method characterized by using as seed crystals a crystalline layered silicate (hereunder abbreviated as PLS), the chemical composition of which is represented by  $[(Si_{18}-$

$x \cdot O_{38}) \cdot M_y (TMA)_z \cdot (H_2O)_w]$  (wherein TMA is a tetraalkylammonium cation, M is a cation of an alkali metal, x satisfies  $0 \leq x \leq 1.2$ , y satisfies  $0.5 \leq y \leq 1.5$ , z satisfies  $6 \leq z \leq 8$  and w satisfies  $0.02 \leq w \leq 1.5$ ), and having as the basic structure thereof a single-layer silicate skeleton comprising one-dimensional micropores nanometers in size formed by a network of covalent bonds between Si and O atoms, condensing the Si-OH groups in the PLS to converting the PLS to CDS-1 having a geometrical crystal structure (atomic arrangement) comprising silicon 5-member and 8-member rings, and thereby forming a zeolite membrane on a support.

28. The zeolite membrane manufacturing method according to Claim 27, wherein a PLS membrane is formed using PLS seed crystals.

29. The zeolite membrane manufacturing method according to Claim 27, wherein the support is a porous base of an inorganic porous body, metal or metal oxide.

30. The zeolite membrane manufacturing method according to Claim 28, wherein the PLS membrane is heated to 300°C to 800°C to condense the Si-OH groups in the PLS and convert to CDS-1.

31. The zeolite membrane manufacturing method according to Claim 30, wherein the PLS membrane is heated under reduced pressure.

32. The zeolite membrane manufacturing method according to Claim 28, wherein the PLS membrane is formed by hydrothermal synthesis at a temperature of 140 to 170°C.

33. The CDS-1 zeolite membrane manufacturing method according to Claim 27, wherein CDS-1 crystals synthesized from PLS are first applied to a support, and a membrane is then formed by secondary growth of the crystals.

34. A method for manufacturing  $\epsilon$ -caprolactam from cyclohexanone oxime  $\epsilon$ -caprolactam, characterized in that a zeolite (CDS-1) having the chemical composition represented by  $[(\text{Si}_{36-x}\text{T}_y\cdot\text{O}_{72})\cdot\text{M}_z]$  (wherein M is a cation of an alkali metal such as Li, Na, K or Rb, T represents Al, Ga, Fe and Ce as skeleton substituting elements, x satisfies  $0 \leq x \leq 3.0$ , y satisfies  $0 \leq y \leq 1.0$  and z satisfies  $0 \leq z \leq 3.0$ ), and having a micropore structure made up of covalent bonds between Si and O atoms and a geometric crystal structure (atomic arrangement) comprising silicon 5-member and 8-member rings is used as a catalyst.

35. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein CDS-1 obtained by dehydration polycondensation at atmospheric pressure is used.

36. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein CDS-1 obtained by

dehydration polycondensation at a heating temperature of 300 to 800°C is used.

37. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein CDS-1 obtained by dehydration polycondensation with a rate of temperature rise of 0.1 to 10°C/minute is used.

38. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein CDS-1 obtained by treating the crystalline layered silicate compound which is the precursor with a group 6 transitional metal oxide in the CDS-1 synthesis process is used.

39. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein the lattice spacing  $d$  (Å) in the powder x-ray diffraction pattern of the CDS-1 exhibits at least the diffraction peaks given in Table 6 below.

Table 6

$d(\text{\AA})$	Relative strength (peak)
$9.17 \pm 0.05$	100
$6.86 \pm 0.05$	35
$6.11 \pm 0.05$	5
$5.50 \pm 0.05$	4
$4.58 \pm 0.05$	3
$4.44 \pm 0.05$	7
$4.35 \pm 0.05$	7

4.09±0.05	6
3.88±0.05	8
3.81±0.05	9
3.68±0.05	3
3.43±0.05	16
3.41±0.05	18
3.31±0.05	8
3.24±0.05	9

40. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein the CDS-1 has micropores with a mean pore size of 0.483 nm or more based on physical adsorption and a volume of 0.6 cc/g or more.

41. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein the CDS-1 used in the Beckmann rearrangement reaction is cation exchanged or hydrogen ion exchanged.

42. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein the reaction temperature in the method for manufacturing  $\epsilon$ -caprolactam from cyclohexanone oxime is 150 to 500°C.

43. The method for manufacturing  $\epsilon$ -caprolactam according to Claim 34, wherein the WHSV of the cyclohexanone oxime is between 0.001 h<sup>-1</sup> and 20.0 h<sup>-1</sup>.